

4-Keto-8-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XIb).—The introduction of the butyronitrile side chain into the preceding keto ester (40 g.) and the hydrolysis and decarboxylation of the resulting product were carried out exactly as described for the preparation of Xa. From the reaction mixture there were isolated 20 g. (50%) of the keto acid, 2–3 g. of phenolic material and 12 g. of 5-methoxy-1-tetralone. The γ -(1-keto-5-methoxy-1,2,3,4-tetrahydro-2-naphthyl)-butyric acid (Xb) after evaporative distillation under reduced pressure and recrystallization from ether–petroleum ether melted at 107°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.70; H, 6.87. Found: C, 68.70; H, 6.95.

Ten grams of the keto acid was converted into its methyl ester, the ketone group was reduced by aluminum isopropoxide, and the product was dehydrated and hydrolyzed as described for XIa. The γ -(5-methoxy-3,4-dihydro-2-naphthyl)-butyric acid (XIb) was recrystallized from ether–petroleum ether; yield, 6.5 g. (70%); m. p. 126–127°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 72.17; H, 7.23. Found: C, 72.23; H, 7.17.

Cyclization of 4 g. of the acid XIb was carried out according to the procedure described for XIIa. After sublimation under reduced pressure, the 4-keto-8-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XIb) crystallized from methanol in colorless prisms; yield, 1.5 g.; m. p. 124–125°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.00. Found: C, 78.73; H, 6.81.

A sample of the ketone was hydrogenated to the alcohol in the presence of platinum oxide and the product was heated at 300° for fifteen minutes with palladium-on-

charcoal. The resulting 1-methoxyphenanthrene after sublimation and recrystallization from methanol melted at 103° alone and when mixed with an authentic specimen of the compound.

γ -(1-Methyl-5-methoxy-3,4-dihydro-2-naphthyl)-butyric Acid.—To a solution of 2.6 g. of the methyl ester of Xb in 50 cc. of anhydrous ether was added a solution of methylmagnesium iodide prepared from 1.3 g. of methyl iodide in 25 cc. of ether. The product of hydrolysis was dehydrated with potassium acid sulfate and hydrolyzed with alcoholic potassium hydroxide. The resulting acid crystallized from ether–petroleum ether in colorless prisms; m. p. 108–109°; yield, 0.65 g.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.85; H, 7.70. Found: C, 74.03; H, 8.09.

Cyclization of the acid chloride with stannic chloride was not successful.

Summary

The Reformatsky reaction involving the use of methyl γ -bromocrotonate has been applied to 1-decalone, 1-tetralone and 2-methyl-2-carbomethoxycyclohexanone. From the products cyclic ketones were synthesized.

Two other cyclic ketones were prepared by the method involving in the first step the introduction of a butyric acid side chain into a cyclic β -keto ester.

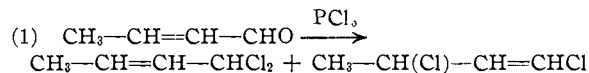
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Allylidene Halides. I. The Dichlorobutene Prepared from Crotonaldehyde

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Phosphorus pentachloride reacts with α,β -unsaturated aldehydes and ketones to form allylidene chlorides. Oftentimes, however, the allylic isomer of the expected dichloride is obtained; and in some cases only the allylic isomer has been isolated.¹ The product of the reaction of crotonaldehyde with phosphorus pentachloride was first described as 1,1-dichloro-2-butene.² Later^{1b} it was reported on the basis of Raman spectra measurements that the product also contained 1,3-dichloro-1-butene (see equation 1). However, the boiling points of the isomers were too close to permit their separation by fractionation.



In connection with studies of the relative reactivities of different allylic halides underway in this Laboratory it was desired to obtain further information on the composition of this dichloride mixture. This report presents the results of experiments performed in an attempt to secure such information.

(1) (a) Kirmann, Pacaud and Dosque, *Bull. soc. chim.*, [5] 1, 860 (1934); (b) Kirmann, *Compt. rend.*, **199**, 1228 (1934); (c) Churbakov, *J. Gen. Chem. U.S.S.R.*, **10**, 977 (1940); (d) Straus and Berkow, *Ann.*, **401**, 121 (1913).

(2) Kekulé, *Ann.*, **162**, 98 (1872).

Oxidation of the Dichloride.—In agreement with Kirmann^{1b} it was found that the dichlorobutene prepared from crotonaldehyde distilled over a range of a few degrees but could not be separated into fractions with the apparatus available. A sample of the distillate was subjected to oxidative degradation with potassium permanganate in neutral solution.^{3,4} Reasonably pure α -chloropropionic acid was isolated from the reaction product, and no significant quantity of dichloroacetic acid could be isolated. This seemed a good indication that the dichloride was actually largely 1,3-dichloro-1-butene.

1-Chloro-1-buten-3-ol.—Supporting, though less conclusive, evidence that the dichloride was largely 1,3-dichloro-1-butene was obtained by comparison of the differences in physical properties of the dichloride and those of 1-chloro-1-buten-3-ol with those recorded⁵ for 1,3-dichloropropene and 3-chloro-2-propen-1-ol. These differences

(3) The method was similar to that used by Ingold and Smith, *J. Chem. Soc.*, 2752 (1931).

(4) Although ozonization procedures have been used in studying structures of similar compounds,¹ the work of Young, McKinnis, Webb and Roberts, *THIS JOURNAL*, **68**, 293 (1946), shows that ozonization of allylic compounds may lead to the formation of abnormal products. It is, of course, not entirely out of the question that permanganate oxidation might be similarly misleading.

(5) Hatch and Moore, *ibid.*, **66**, 285 (1944).

are compared in Table I.⁶ The chlorobutenol was prepared by stirring the dichlorobutene with an aqueous suspension of silver oxide. Any 1-chloro-2-buten-1-ol formed in this reaction would be expected to decompose immediately to form crotonaldehyde, but no aldehyde was isolated. Treatment of the chlorobutenol with concentrated hydrochloric acid gave a dichlorobutene the physical properties of which were very close to those of the dichloride prepared from crotonaldehyde.

TABLE I
PHYSICAL PROPERTIES OF DICHLOROBUTENE AND THE
CHLOROBUTENOL

	B. p., °C. (mm.)	n_D	d
Dichlorobutene ^a	71.9 (199)	$n_D^{24.5}$ 1.4620	d_4^{24} 1.134
1-Chloro-1- buten-3-ol	107-109 (201)	$n_D^{24.5}$ 1.4581	d_4^{24} 1.079
Δ^b	36	0.0039	0.055
1,3-Dichloropro- pene(α) ^c	104.3	n_D^{20} 1.4682	d_4^{20} 1.224
3-Chloro-2-pro- pen-1-ol(α) ^c	146.3	n_D^{20} 1.4638	d_4^{20} 1.177
Δ^b	42	0.0044	0.047

^a Prepared from the chlorobutenol and hydrochloric acid. ^b Differences in properties between the dichloride and the chloroalcohol. ^c These are the stereoisomers designated as α .⁵ Comparison between the β isomers gives similar results. As yet no evidence has been found as to whether or not the corresponding butene derivatives are a mixture of *cis-trans* isomers. Further comment on this point is made later.

Kinetic Studies.—3-Chloro-1-butene, a secondary allylic halide, is very reactive with respect to solvolysis as compared to the allylidene halide, 3,3-dichloropropene.^{7,8} It therefore seemed reasonable to suspect that the secondary allylic halide, 1,3-dichloro-1-butene might undergo solvolysis more rapidly than 1,1-dichloro-2-butene⁹ and that an estimate of the composition of the dichlorobutene mixture might be obtained by a study of its solvolysis rate. Accordingly the rate of production of hydrogen ion in 50 volume per cent. aqueous ethanol solutions of the dichlorobutene mixture was followed at 25°. The major

(6) Such a comparison as this would be of no value unless there were some assurance that there was a significant difference in the physical properties of 1,3-dichloro-1-butene and 1,1-dichloro-2-butene. Actually the boiling points of the two isomers do appear to be close. However data recorded in Table III indicate that there is an appreciable difference in the refractive indices and densities of the two isomers. A sample which kinetic analysis indicated was 90% 1,3-dichloro-1-butene (Run V) had a refractive index 0.0027 unit lower and a density 0.015 unit lower than a sample of pure 1,3-dichloro-1-butene (Run VI). It thus seems reasonable to suspect that there would be a large enough difference in these two constants for the pure isomers to justify the above comparison.

(7) Young and Andrews, *THIS JOURNAL*, **66**, 421 (1944).

(8) Unpublished data obtained in this Laboratory show that the first order solvolysis constant of 3,3-dichloropropene in 50 volume per cent. aqueous ethanol at 25° is 7×10^{-4} hours⁻¹ as compared to a value of 0.04 hrs.⁻¹ for 3-chloro-1-butene.

(9) The data so far available on the reactivity of halogen in allylidene halides is, however, insufficient to permit unqualified prediction of the relative reaction rates of the dichlorobutenes: (a) Olivier and Weber, *Rec. trav. chim.*, [4] **53**, 869 (1934); (b) Hughes, *Trans. Faraday Soc.*, **37**, 625 (1941).

portion of the dichloride reacted very rapidly, and over long periods of time a total of one mole of hydrogen ion was liberated per mole of original dichloride according to equation (2) in which SH represents the solvent.



First order rate constants calculated from the integrated form (3) of equation (4) usually diminished as a function of time during any one run. This fact is in accord with the assumption that two isomers were present, one of which reacted faster than did the other.

$$(3) \quad k = \frac{2.303}{t} \log [\text{BuCl}_2 / (\text{BuCl}_2 - \text{H}^+)]$$

$$(4) \quad \frac{d\text{H}^+}{dt} = k(\text{BuCl}_2 - \text{H}^+)$$

BuCl₂ = initial dichloride concn.
H⁺ = hydrogen ion concn. at time *t*

The correct rate expression would then be⁵

$$(5) \quad \frac{d\text{H}^+}{dt} = k_1(A - x) + k_2(B - y)$$

in which *A* and *B* are the initial concentrations of the two allylic isomers and *x* and *y* are the concentrations of hydrogen ion liberated respectively by *A* and *B* at time *t*. Assuming that 1,1-dichloro-2-butene would have a low rate constant, equation

TABLE II
THE SOLVOLYSIS OF DICHLOROBUTENE IN 50 VOLUME %
AQUEOUS ETHANOL AT 25°^a

	Time, hours	H ⁺ moles/l.	BuCl ₂ - H ⁺ moles/l.	<i>k</i> hours ⁻¹	$\frac{d\text{H}^+}{dt} =$ $k(\text{BuCl}_2 - \text{H}^+)$
Run III	0	0.09014
	0.376	0.01223	.07791	0.392	0.0305
	.658	.01920	.07094	.365	.0259
	1.08	.02880	.06134	.357	.0219
	1.98	.04410	.04604	.340	.0157
	2.48	.05110	.03904	.338	.0132
	3.28	.05940	.03074	.329	.0101
	3.99	.06480	.02534	.318	.0080
	5.63	.07300	.01714	.294	.0050
7.52	.07800	.01214	.267	.0032	
Run V	008231
	0.417	.01002	.07229	.314	.0227
	.667	.01538	.06693	.310	.0207
	1.33	.02726	.05505	.303	.0167
	2.50	.04190	.04041	.286	.0116
	3.83	.05270	.02961	.267	.0079
	23.66	.07200	.01031	.088
	48.33	.07650	.00581	.055
	192	.08250
Run VI	008200
	0.417	.01245	.06955	.397 ^b	.0276
	.667	.01905	.06295	.394	.0248
	1.33	.03315	.04885	.391	.0191
	3.33	.05995	.02205	.395	.0087
	19.7	.08280
	27.1	.08300

^a In plotting $d\text{H}^+/\text{dt}$ against H^+ it was found that all points except the first fit very closely to a straight line. The first point was always slightly high owing to traces of hydrogen chloride in the samples. ^b Mean value of $k = 0.393$ as based on nine observations.

TABLE III
 PROPERTIES OF THE DICHLOROBUTENE SAMPLES

Run	Physical constants of BuCl ₂ ^a				Rate data			
	°C.	B. p., Mm.	<i>n</i> _D	<i>d</i>	Orig. BuCl ₂ concn., mole/l.	<i>k</i> ₁ hours ⁻¹	<i>A</i> mole/l.	% <i>A</i> in BuCl ₂
I	70.0-73.0	200	<i>n</i> ²² _D 1.4620	<i>d</i> ₄ ²² 1.1249	0.08026	0.390	0.0735	92
II	70.0-73.0	200	<i>n</i> ²² _D 1.4620	<i>d</i> ₄ ²² 1.1249	.05340	.422	.0462	87
III	70.0-72.0	199	<i>n</i> ²⁰ _D 1.4640	<i>d</i> ₄ ²⁰ 1.1376	.09014	.386	.0855	95
IV ^b	70.0-72.0	199	<i>n</i> ²⁰ _D 1.4640	<i>d</i> ₄ ²⁰ 1.1376	.08296	.395	.0740	89
V ^c	73.0-75.0	204	<i>n</i> ²⁰ _D 1.4621	<i>d</i> ₄ ²⁰ 1.1247	.08231	.359	.0738	89.5
VI ^c	75.0-76.0	204	<i>n</i> ²⁰ _D 1.4648	<i>d</i> ₄ ²⁰ 1.1393	.08200	.400 ^d	.0815	99.5
VII	71.9 ^e	199	<i>n</i> ²¹ _D 1.4638	<i>d</i> ₄ ²⁴ 1.1341	.08083	.421 ^f	.0785	97.5

^a Kirrinnann^{1b} reported properties as follows: b. p. 120-123°, *d*²⁰ 1.130, *n*²⁰_D 1.464; b. p. 124-125°, *d*¹⁸ 1.140, *n*¹⁸_D 1.466. ^b Sodium hydroxide used in this run (initial concn. 0.0548 *M*). ^c Runs V and VI were made respectively on the low (21.4 g.) and high (19.3 g.) boiling cuts obtained from one dichlorobutene preparation. The distillation temperatures seemed slightly high for these samples. This probably resulted from slight error in pressure measurement. ^d Average value of *k* (equation 4) was 0.393. ^e Dichloride prepared from 1-chloro-1-buten-3-ol. ^f Average value of *k* was 0.398.

(5) reduces to (6), in which *A* is the initial concentration of 1,3-dichloro-1-butene.

$$(6) \quad dH^+/dt = k_1(A - H^+)$$

If this expression is correct, a plot of values of dH^+/dt for the rapid phase of the reaction against the corresponding hydrogen ion concentrations as ordinates should give a straight line, the slope of which is $-k_1$ and the ordinate intercept of which is k_1A . The values of dH^+/dt may be calculated by substitution of *k* values obtained from equation (3) into equation (4).¹⁰

Application of this kinetic method to the analysis of several different dichlorobutene samples gave surprisingly good results. In every case the graphical analysis gave a straight line plot, and the *k*₁ values for the several runs were in close agreement. The data for three typical runs are summarized in Table II. A summary of the values of *k*₁ and the per cent. 1,3-dichloro-1-butene (*A*) in the several samples are listed in Table III along with the physical properties of the samples.

Runs I and II were made with samples of the total distillate of the product of reaction of crotonaldehyde and phosphorus pentachloride. Runs III and IV were made with a dichloride sample from a different preparation. Slight differences in the physical properties of the two samples probably result from slight variations in the composition with respect to allylic isomers. An average of the data from these four runs indicated that the mixture was about 91% 1,3-dichloro-1-butene. Runs V and VI were made, respectively, with the lower and higher boiling portions of the distillate of one dichlorobutene preparation.

(10) The use of equations (3) and (4) to obtain values of dH^+/dt is only an approximation procedure since these equations do not exactly represent the rate law. However in the case under consideration, in which *A* is about 90% of total dichlorobutene, the values of dH^+/dt calculated by this method for the early phase of the reaction are accurate to within a few per cent. These values may be used with reasonable accuracy to determine *k*₁ and *A*. Theoretically the correct procedure to obtain values of dH^+/dt would involve measuring the slopes of the curve obtained by plotting hydrogen ion concentration against time. The errors inherent in measuring the slopes limit the accuracy to the point at which the use of the simpler approximation procedure becomes practical. In one case the values of dH^+/dt calculated by equations (3) and (4) were checked against those obtained by graphing. The agreement was reasonably good.

The higher boiling material appeared to be pure 1,3-dichloro-1-butene, while the lower boiling fraction appeared to contain about 10% of the unreactive isomer. Actually the values of *k* calculated from equation (3) for Run VI did not diminish appreciably. Their average value, 0.393, agreed well with the value of *k*₁ = 0.400 obtained by graphical methods. Run VII was made with the dichloride prepared from 1-chloro-1-buten-3-ol. This material also appeared to be reasonably pure 1,3-dichloro-1-butene.¹¹

All of the evidence collected indicates that the dichlorobutene prepared from crotonaldehyde is 1,3-dichloro-1-butene contaminated with a few per cent. of what appears most likely to be 1,1-dichloro-2-butene. It might be possible to isolate the latter compound from the mixture in pure form by controlled destructive solvolysis of the former. However, in view of the limited solubility of the dichloride in the solvent used and the small amounts of 1,1-dichloro-2-butene in the mixture, the isolation of any sizable quantity would be a most difficult task.

The Relative Reactivities of 1,3-Dichloro-1-butene and 3-Chloro-1-butene.—The reactivity of 1,3-dichloro-1-butene seems to be in accord with the generalizations of Hughes¹² regarding the mechanisms of nucleophilic substitution reactions of allylic systems. The solvolysis rate constant of the dichloride is about ten times that of 3-chloro-1-butene. If one accepts the resonance form, $\text{CH}_2=\text{CH}(\text{Cl})-\ddot{\text{C}}\text{H}-\text{CH}=\text{Cl}^+$, as contributing

(11) It should be noted that both of the isomeric dichlorobutenes may exist in *cis* and *trans* forms, though no separation of such isomers could be accomplished with the apparatus used. It might be argued that the unreactive fraction of the dichloride was actually a stereoisomer of 1,3-dichloro-1-butene rather than 1,1-dichloro-2-butene. However, it seems unlikely that there would be a pronounced difference in the rate of solvolysis of the two stereoisomers. It is noteworthy that there is little difference in the rates of hydrolysis of the *cis* and *trans* 1,3-dichloropropenes [Hatch and Roberts, *This Journal*, **68**, 1196 (1946)]. Also the Raman data of Kirrinnann^{1b} indicated that the lower boiling portion of the dichlorobutene was the richer in 1,1-dichloro-2-butene, which is in accord with the observations of Runs V and VI. Thus while it is not clear whether the 1,3-dichloro-1-butene under investigation is a mixture of *cis* and *trans* isomers, it would seem that the unreactive material obtained with it is 1,1-dichloro-2-butene.

(12) Ref. 9b, p. 627.

to the structure of the dichloride, it might be expected that the rate determining separation of chloride ion from the secondary carbon would be facilitated. The solvolysis rates of both the mono- and dichlorobutene are independent of hydroxide ion (Run IV, Table III).⁷

The rate of reaction of 1,3-dichloro-1-butene with sodium ethoxide in absolute ethanol was also followed (Table IV). The bimolecular rate constant was found to be about four times as large as that for the same reaction of 3-chloro-1-butene. Probably the bimolecular reaction is favored by the inductive effect of the chlorine attached to the vinyl group in 1,3-dichloro-1-butene.

TABLE IV

BIMOLECULAR REACTION OF 1,3-DICHLORO-1-BUTENE AND SODIUM ETHOXIDE AT 25^oa,b

Time, hours	RCl ₂ mole/l.	NaOC ₂ H ₅ mole/l.	k hr. ⁻¹ mole ⁻¹ l.
0	0.2190	0.1220	...
46.5	.2012	.1042	0.016
70.0	.1950	.0980	.015
93.7	.1892	.0922	.015
117.6	.1840	.0870	.015
147.7	.1785	.0815	.014
189.5	.1705	.0735	.014

^a The product was assumed to be 1-chloro-3-ethoxy-1-butene as reported by Kirrmann^{1b} for this reaction.

^b The dichloride sample used was the same as that employed in Run VI, Table III.

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Experimental

The Dichlorobutene.—Ninety ml. (1.1 mole) of crotonaldehyde was added dropwise with stirring to 227 g. (1.09 mole) of phosphorus pentachloride in an ice-cooled flask over a forty-five minute period. After standing overnight at room temperature the product was hydrolyzed by adding 200 ml. of water dropwise over a five- to eight-hour period. The yield was diminished considerably if the mixture was allowed to warm much above room temperature during hydrolysis. The organic matter was then distilled from the mixture and washed with water and dried over potassium carbonate. The crude product was distilled quickly at 200 mm. pressure and was then distilled carefully under reduced pressure through a two-foot column packed with glass helices. The physical properties of the several preparations are given in Table III; maximum yield, 57 g. (42%). The product decomposed slightly if distilled at atmospheric pressure (b. p. about 120^o).

Permanganate Oxidation of the Dichlorobutene.—Ten grams (0.08 mole) of dichlorobutene (see Table III, Run III for physical properties), 20 g. of potassium permanganate and 20 g. of magnesium sulfate heptahydrate were mixed in 400 cc. of water. The mixture was stirred vigorously for one hour at room temperature. The mixture was then heated slowly to 50^o with stirring and was allowed to cool overnight. The inorganic solids were removed by filtration. The colorless filtrate was extracted with ether, and the acids were removed from the ether by extraction with dilute sodium carbonate. The basic solution was acidified with sulfuric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate. After removal of the ether, the residue was distilled under reduced pressure. Two grams of α -chloropropionic acid of b. p. 75^o (13 mm.) and n_D^{20}

1.4341 was obtained. *Anal.* Calcd. for C₂H₄(Cl)COOH: neut. equiv., 108.5. Found: neut. equiv., 111.0. Chloride *Anal.* (A weighed sample was refluxed one hour with 100 ml. of 10% aqueous sodium hydroxide, and the resultant solution was analyzed by a gravimetric silver chloride determination.) Calcd.: Cl, 32.7. Found: Cl, 33.2. Both analyses gave slightly high results, and it is possible that the sample contained small amounts of dichloroacetic acid.

1-Chloro-1-buten-3-ol.—Silver oxide freshly prepared from 80 g. (0.47 mole) of silver nitrate was suspended in 500 ml. of water. To the well stirred mixture 50 g. (0.40 mole) of dichlorobutene was added dropwise over a one-half hour period. The mixture was stirred for an additional one and one-half hours. The silver chloride was removed by filtration and the filtrate was distilled to remove the chlorobutenol. The alcohol was salted from the distillate and dried over potassium carbonate. The crude product was distilled under reduced pressure from a modified Claisen flask; yield 18.8 g. (44%). The product reacted vigorously with acetyl chloride. The properties other than those listed in Table III were as follows: M_D calcd. 26.60; M_D found 26.96. *Anal.* Calcd.: Cl, 33.3. Found: Cl, 32.6. The chloride analysis was performed by oxidation of a weighed sample of the alcohol with aqueous potassium permanganate. The excess permanganate was reduced by the addition of allyl alcohol. The manganese dioxide was filtered from the mixture, and the acidified filtrate was analyzed for chloride ion by the usual gravimetric procedure.

Conversion of 1-Chloro-1-buten-3-ol to Dichlorobutene.—Fifty ml. of concentrated hydrochloric acid was added to 16.5 g. (0.15 mole) of the alcohol contained in an ice-cooled flask. The mixture was allowed to warm to room temperature and was then shaken occasionally over a three-hour period. The mixture was diluted with water. The organic phase was separated, washed with water and dried over potassium carbonate. The product was distilled under reduced pressure in an all-glass system. The distillate weighed 12.7 g., yield 68%.

Solvolysis Rates of the Dichlorobutene Samples.—The solvent used was 50 volume per cent. aqueous ethanol, and the rate measurements were made at 25^o in a manner similar to that previously described.⁷ In the runs in which no sodium hydroxide was introduced into the reaction mixture the samples taken were run into chilled flasks and titrated with alcoholic sodium hydroxide using methyl red indicator. Aqueous sodium hydroxide was unsatisfactory for the titration owing to the sensitivity of the reaction rate to water concentration. In the run in which sodium hydroxide was used the samples were titrated with alcoholic hydrogen chloride.

The Reaction of the Dichlorobutene with Sodium Ethoxide in Absolute Ethanol.—The rate was followed at 25^o in essentially the same manner as described previously.⁷ Alcoholic hydrogen chloride and methyl red indicator were used in the titration of samples. Since the end-points were poor, the rate constants were calculated only to two significant figures.

Summary

The dichlorobutene prepared by the reaction of crotonaldehyde with phosphorus pentachloride has previously been characterized by Raman spectra measurements as a mixture of 1,3-dichloro-1-butene and 1,1-dichloro-2-butene. The results of studies of permanganate oxidation of the dichloride mixture and of its rate of solvolysis in aqueous ethanol indicate that the material is about 90% 1,3-dichloro-1-butene. The reactivity of the dichloride with respect to nucleophilic reagents seems to be in accord with the results of similar studies for other allylic halides.